

# **Uptake of nitrate and sulfate on dust aerosols during TRACE-P**

**C. E. Jordan<sup>1</sup>, J. E. Dibb<sup>2</sup>, B. E. Anderson<sup>1</sup>, and H. E. Fuelberg<sup>3</sup>**

<sup>1</sup>NASA Langley Research Center

MS 483

Hampton, VA 23681

<sup>2</sup>Climate Change Research Center

Institute for the Study of Earth Oceans and Space

University of New Hampshire

Durham, NH 03824

<sup>3</sup>Department of Meteorology

Florida State University

Tallahassee, FL 32306

30 October 2002

submitted to Journal of Geophysical Research – Atmospheres

for consideration for TRACE-P Special Issue

## ABSTRACT

Aerosol data collected near Asia on the DC-8 platform during TRACE-P has been examined for evidence of uptake of  $\text{NO}_3^-$  and  $\text{SO}_4^{=}$  on dust surfaces. Data is compared between a sector where dust was predominant, to a sector where dust was less of an influence. Coincident with dust, were higher mixing ratios of anthropogenic pollutants.  $\text{HNO}_3$ ,  $\text{SO}_2$ , and CO were higher in the dust sector than the non-dust sector by factors of 2.7, 6.2, and 1.5, respectively. The co-location of dust and pollution sources allowed for the uptake of  $\text{NO}_3^-$  and nss- $\text{SO}_4^{=}$  on the coarse dust aerosols, increasing the mixing ratios of these particulates by factors of 5.7 and 2.6 on average. The abundance of nss- $\text{SO}_4^{=}$  was such that all of the  $\text{NH}_4^+$  present could be accommodated with plenty left over to react with dust  $\text{CaCO}_3$ , which suggests that the enhanced  $\text{NO}_3^-$  was not in fine mode  $\text{NH}_4\text{NO}_3$ . Uptake of  $\text{NO}_3^-$  and nss- $\text{SO}_4^{=}$  appeared to be limited by the amount of precursor gases, requiring  $> 50 \text{ nmol/m}^3$  and  $> 100 \text{ nmol/m}^3$  for  $\text{HNO}_3$  and  $\text{SO}_2$ , respectively, before these particulate species became enhanced in the presence of dust. Particulate  $\text{NO}_3^-$  (p- $\text{NO}_3^-$ ) constituted 54% of the total  $\text{NO}_3^-$  (t- $\text{NO}_3^-$ ) on average, reaching a maximum of 72% in the dust sector. In the non-dust sector, p- $\text{NO}_3^-$  contributed 37% to t- $\text{NO}_3^-$ , likely due to the abundance of sea salts there. In two other sectors where the influence of dust and sea salt were minimal, p- $\text{NO}_3^-$  accounted for  $< 15\%$  of t- $\text{NO}_3^-$ .

## INTRODUCTION

Using 40 years of dust storm records, Sun et al. [2001] describe how dust is transported out of China. These dust storms occur predominantly in spring [Liu, 1985, Sun et al., 2001] and are due to cold air outbreaks which cause frontal systems and the Mongolian cyclonic depression. About 78% of dust storms are associated with the Mongolian cyclone with the remainder associated solely with the passage of cold fronts [Sun et al., 2001]. There are two dominant source regions of dust in east Asia, gobi deserts in Mongolia and northern China, and the Taklimakan Desert in western China. Due to the mountains surrounding the Taklimakan, dust can only be exported out of this region when strong easterlies loft dust above 5 km in altitude (the height of the mountains). At these heights, this dust becomes entrained in the jet stream and may then be transported long distances over the Pacific Ocean and to North America. Dust from the gobi deserts of Mongolia and northern China on the other hand, is generally lofted to altitudes  $< 3$  km and then transported in a southeasterly direction, depositing dust on the Loess Plateau, eastern Asia, and the western Pacific (Figure 1, Sun et al., [2001]).

The mineralogy of loess at its source consists primarily of quartz ( $\text{SiO}_2$ ), feldspars, micas, clays, carbonates (primarily  $\text{CaCO}_3$ ), and several minor minerals [Pye, 1987; Gao and Anderson, 2001]. The carbonate content is relatively constant at 12% by weight in loess, dust, and ground surface samples [Derbyshire et al., 1998]. Nishikawa et al. [1991] found weight fractions of  $\text{SO}_4^{=}$  in soils of arid regions of China ranged from  $< 0.01\%$  to  $0.46\%$ , insufficient to account for the high fraction of  $\text{SO}_4^{=}$  in dust downwind of these regions. Individual dust particles from five dust storms in Beijing examined by Zhang and Iwasaka [1999] showed very little water soluble  $\text{SO}_4^{=}$  on the surface of these

particles. Only about 15% of the particles had a sulfur peak, even fewer, 11%, showed any  $\text{NO}_3^-$ . This suggests little chemical alteration takes place prior to reaching Beijing. Yet, samples collected in Qingdao, 500 km southeast of Beijing showed 50-80% of the coarse particles ( $> 2 \mu\text{m}$  diameter) were coated with  $\text{SO}_4^{=}$  [Parungo et al., 1995]. This chemical alteration then must occur downstream from Beijing.

The presence of  $\text{CaCO}_3$  in Asian dust is important because it reacts with acids such as sulfuric and nitric acid. In this way, dust particles may be chemically altered from their original composition at their source. Assuming the dust particles travel along a path where anthropogenic S and N sources are important, the surface area provided by the dust particles may lead to significant alteration of the air mass chemistry as  $\text{SO}_2$  and  $\text{HNO}_3$  transfer from gas to particulate phase [Zhang et al., 1994; Xiao et al., 1997; Song and Carmichael, 2001a&b]. The presence of these acidic ions on dust can change the solubility of the aerosol from hydrophobic to hydrophilic [Song and Carmichael, 2001a].

Evidence of  $\text{SO}_4^{=}$  and  $\text{NO}_3^-$  on dust is found in studies of individual particles [e.g., Wu and Okada, 1994; Parungo et al., 1995; Gao and Anderson, 2001] as well as studies of bulk aerosol composition [e.g., Choi et al., 2001; Kim and Park, 2001] and precipitation [e.g., Minoura et al., 1998]. Individual particles show both  $\text{NO}_3^-$  and  $\text{SO}_4^{=}$  inclusions along with  $\text{CaCO}_3$ , as well as particles where all of the  $\text{CO}_3^{=}$  has been replaced [Wu and Okada, 1994; Parungo et al., 1995; Gao and Anderson, 2001]. Bulk aerosols from dust events show dominant water soluble ions are  $\text{SO}_4^{=}$ ,  $\text{NO}_3^-$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$  [Choi et al.,

2001; Kim and Park, 2001]. Where size resolved data is available,  $\text{NO}_3^-$  and  $\text{SO}_4^{=}$  are found primarily in the coarse fraction associated with  $\text{Ca}^{2+}$  during dust events [Kim and Park, 2001]. In the absence of dust,  $\text{SO}_4^{=}$  is primarily in the fine mode, while  $\text{NO}_3^-$  can be associated with either  $\text{NH}_4^+$  in the fine mode [Kim and Park, 2001; Song and Carmichael, 2001a] or  $\text{Na}^+$  in the coarse mode [Song and Carmichael, 2001a]. In precipitation in Japan, the highest average concentrations of  $\text{NO}_3^-$ ,  $\text{SO}_4^{=}$ , and  $\text{Ca}^{2+}$  are observed during Kosa (dust storm) events [Minoura et al., 1998]. The low pH of precipitation during these dust events is attributed to the large amounts of acidic ions on the Kosa particles scavenged by the precipitation [Minoura et al., 1998]. By the time dust particles reach Korea and Japan, about 75% of the carbonate has been displaced by  $\text{SO}_4^{=}$  and  $\text{NO}_3^-$  [Nishikawa et al., 1991].

Various modeling studies have estimated the degree to which heterogeneous reactions contribute to the production of coarse mode  $\text{SO}_4^{=}$  and  $\text{NO}_3^-$ . Chameides and Stelson [1992] estimated > 70% of  $\text{SO}_4^{=}$  formed by heterogeneous reactions. Using a regional 3-D model for the period March 1-14, 1994, Xiao et al. [1997] estimated chemical conversion of  $\text{SO}_2$  in the presence of dust contributed 20-40% to total  $\text{SO}_4^{=}$  production in East Asia. Song and Carmichael [2001a] also using a regional 3-D model, found heterogeneous reactions account for 10-40% of  $\text{SO}_4^{=}$  production in dust plumes, and 10-80% in sea salt dominant regions. They attribute the greater production of  $\text{SO}_4^{=}$  on sea salt versus dust to the dust mass distribution having a larger coarse fraction than sea salt.

Dentener et al. [1996] looked at irreversible reactions of  $\text{HNO}_3$ ,  $\text{N}_2\text{O}_5$ ,  $\text{NO}_3$ ,  $\text{HO}_2$ ,  $\text{O}_3$ , and  $\text{SO}_y$  on dust surfaces. They predicted that a substantial fraction of  $\text{SO}_4^{2-}$  is associated with mineral aerosol. They also found that an even larger fraction of gas phase  $\text{HNO}_3$  may be neutralized by mineral aerosol. Phadnis and Carmichael [2000] predict > 70% of gas-phase  $\text{HNO}_3$  is partitioned onto dust over the Gobi Desert, while 10-70% of  $\text{HNO}_3$  ends up in particulate phase over the rest of East Asia. Song and Carmichael [2001a] predict 10-50% of  $\text{HNO}_3$  partitioned into  $\text{NO}_3^-$  in the boundary layer, with this partitioning exceeding 70% in dust and sea salt plume centers. In the free troposphere, they predict 10-30% of  $\text{HNO}_3$  partitioned into particulate phase, increasing to > 50% in dust plume centers. Song and Carmichael's model [2001a] also suggests that while  $\text{NO}_3^-$  resides primarily in coarse mode, that in regions with abundant  $\text{NH}_3$  and  $\text{HNO}_3$ , fine mode  $\text{NH}_4\text{NO}_3$  may be found. The region where this is most likely to occur is around the lower Huang river, where there is high population density and agricultural activity [Song and Carmichael, 2001a]. Underwood et al. [2001] studied the uptake of  $\text{NO}_2$  and  $\text{HNO}_3$  in the laboratory coupled with model calculations. They found that while uptake of  $\text{NO}_2$  does not appear to be significant, uptake of  $\text{HNO}_3$  is significant, with mixing ratios reduced by 30%. They note that this fraction is likely to increase under humid *in situ* conditions versus the dry conditions of their experiment.

As discussed by Sun et al. [2001], we found dust emanating from the Asian continent from a well confined sector [Jordan et al., this issue] during TRACE-P (TRANsport and Chemical Evolution of the Pacific). A thorough comparison of bulk chemical and

physical aerosol properties are made in that paper. Here, we focus on the dust sector, to look for evidence of gas to particle transfer of  $\text{NO}_3^-$  and  $\text{SO}_4^{=}$ .

## APPROACH

Back trajectories coupled with aerosol chemical data were used to classify the DC-8 TRACE-P aerosol data into four groups [Jordan et al., this issue]. The chemical samples were collected over periods ranging from approximately 5 to 35 minutes during level flight legs. The back trajectories were calculated every 5 minutes during level flight legs [Fuelberg et al., this issue]. Thus, an individual aerosol sample might have anywhere from 1 to 7 back trajectories associated with it. Samples that had multiple trajectories which emanated from more than one of the four sectors, were classified as mixed and not used any further in the analysis. The idea was to obtain a set of samples that represented a given sector with as little interference from other sectors as possible. In this way, 77 samples were obtained for the NNW sector, 38 for Channel, 31 for SE Asia, and 47 for WSW.

NNW and Channel trajectories both emanate from northern Asia, with the Channel trajectories bounding the NNW trajectories to the south and west (Figure 2, top panel). The Channel trajectories themselves are bounded to the south by the Tibetan Plateau. WSW trajectories (not shown here) typically reflect high altitude, long range transport from the west as far away as Africa. SE Asia trajectories tend to circle over the western Pacific and southeast Asia. Both of these latter sectors have much lower mixing ratios of

aerosols in general than the two former sectors, making them less appropriate for a comparison which tries to isolate the dust component. For a more extensive discussion of the sampling method and back trajectory calculations, please refer to Jordan et al. [this issue]. A complete discussion of the aerosol properties of each sector appears in that paper. Here, the intention is to use just the Channel and NNW sectors to examine the influence of dust on aerosol chemistry, particularly, the uptake of  $\text{NO}_3^-$  and  $\text{SO}_4^{=}$  on dust surfaces.

## DISCUSSION

Sun et al. [2001] described the pathways of the cold air outbreaks which lead to dust storms, as well as the pathways the suspended dust particles follow once suspended (Figure 1). Pathway I is followed by cold air masses near Lake Baikal which move southward across central Mongolia and China. Pathway II involves cold air masses in the northwest which result in dust storms along the Hexi Corridor (a northwest-southeast trending geographic region which connects the Xinjiang and Gansu Provinces) and gobi deserts in northern China. Pathway III results in dust storms both in the Hexi Corridor and Taklimakan Desert. Most of the cold air outbreaks follow pathway II (41%), followed by pathway III (37%), and pathway I (32%). Sun et al. [2001] then breakdown the routes the suspended dust travels. Routes A, B, and C (Figure 1) carry dust from the gobi deserts in Mongolia and China depositing it en route to Korea, Japan, and the Pacific Ocean. Route B is most common (60%) followed by C (33%), then A (7%). Route D



carries dust out of the Taklimakan Desert to high altitudes where it becomes entrained in the jet stream and is transported long distances downwind [Sun et al., 2001].

During TRACE-P, using aerosol chemistry coupled with back trajectories, we determined the path followed by the majority of the dust observed by the DC-8 [Jordan et al., this issue]. The back trajectories for these dust samples (Figure 2, bottom panel) closely resemble the C and B routes described by Sun et al. [2001] (Figure 1).

In order to investigate the role of dust in heterogeneous uptake of  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ , we compare the dust sector (Channel) to the adjacent sector (NNW). For a description of these sectors, please see Jordan et al. [this issue]. The primary distinction between these sectors is the presence of dust. However, Channel also has higher pollution inputs as well, as evidenced by gas phase species such as  $\text{HNO}_3$  and CO (Table 1). This results in all aerosol species showing higher means in Channel than NNW (Figure 3), except for  $\text{Na}^+$ . The primary source of  $\text{Na}^+$  in the DC-8 measurements is sea salt, hence there is little difference between the mean mixing ratios for these groups.

As discussed in Keene et al. [1986],  $\text{Na}^+$  and  $\text{Mg}^{2+}$  are generally considered the best tracers of sea salt. However, this can become complicated when crustal sources add a significant amount to these species in coastal environments. Comparing the measured ratio of  $\text{Mg}^{2+}/\text{Na}^+$  to the equivalence ratio of 0.227 found in bulk sea water [Wilson, 1975; Keene et al., 1986], one can determine which species to use as the reference sea salt species. If the measured ratio exceeds 0.227, then crustal  $\text{Mg}^{2+}$  is influencing the

measurement. Conversely, if the ratio is less than 0.227, then crustal  $\text{Na}^+$  is interfering with the marine signal. Here, the data closely adheres to the sea salt ratio for the NNW group (Figure 4). However,  $\text{Mg}^{2+}$  is clearly enhanced in Channel, altering the slope significantly from what one would expect for sea salt salt (Figure 4). Thus, for this study,  $\text{Na}^+$  is used as the reference species for sea salt, since it appears less likely to suffer from major deviations from the marine source. However, it is known that  $\text{Na}^+$  is a component of Asian dust [Song and Carmichael, 2001b]. Hence, in calculating the sea salt and non-sea-salt components of the aerosol species reported here, the non-sea-salt species will be somewhat underestimated for the Channel group.

The distribution of  $\text{NO}_3^-$ ,  $\text{HNO}_3$ ,  $\text{nss-Ca}^{2+}$ ,  $\text{Na}^+$ ,  $\text{nss-SO}_4^{=}$ , and  $\text{NH}_4^+$  as a function of altitude show that most species are enhanced at low altitudes (Figure 5). Density ellipses which enclose 90% of the points within each group show Channel mixing ratios enhanced compared to those of NNW. The enhancement of  $\text{NO}_3^-$  may be due to three possible reaction routes: 1) uptake of  $\text{HNO}_3$  by sea salt, 2) uptake of  $\text{HNO}_3$  by alkaline dust, primarily by reaction with  $\text{CaCO}_3$ , or 3) formation of fine mode  $\text{NH}_4\text{NO}_3$ . The first pathway may be eliminated since there is little difference between the availability of  $\text{Na}^+$  between Channel and NNW (Figure 5). Further, several of the high  $\text{NO}_3^-$  samples (circles, Figure 5) appear at low concentrations of  $\text{Na}^+$ . Four of the high  $\text{NO}_3^-$  samples (blue circles, Figure 5) do have high  $\text{Na}^+$  concentrations, however, these samples also have the highest  $\text{nss-Ca}^{2+}$  measured (Figure 5). This suggests the high  $\text{Na}^+$  in these samples is due to crustal dust, rather than sea salt. All of the high  $\text{NO}_3^-$  samples are also high  $\text{nss-Ca}^{2+}$  samples. In addition to the high  $\text{NO}_3^-$  markers (circles), there are many

samples with enhanced dust (red squares, Figure 5). However, these samples do not have enhanced  $\text{HNO}_3$ , which suggests both  $\text{HNO}_3$  and  $\text{nss-Ca}^{2+}$  need to be enhanced to yield enhanced  $\text{NO}_3^-$  via uptake on dust. Another possible explanation for the enhanced  $\text{NO}_3^-$  may be the formation of fine mode  $\text{NH}_4\text{NO}_3$  rather than coarse mode uptake of  $\text{NO}_3^-$ . All of the enhanced  $\text{NO}_3^-$  samples are observed to have enhanced  $\text{NH}_4^+$  as well (Figure 5). Most of the markers also show enhanced  $\text{nss-SO}_4^{=}$  (Figure 5). Hence, both mechanisms 2 and 3 may be important.

Taking  $\text{nss-Ca}^{2+}$  values  $> 100 \text{ neq/m}^3$  to indicate enhanced dust, there are clearly two populations of  $\text{NO}_3^-$  (Figure 6). Samples where  $\text{NO}_3^-$  is  $\geq$  about  $100 \text{ neq/m}^3$  (circles, Figure 6) tend to fall near the 1:1 line, although generally there is excess  $\text{nss-Ca}^{2+}$  compared to  $\text{NO}_3^-$ . The other population is denoted by red squares. For these samples, although  $\text{nss-Ca}^{2+}$  indicates an abundance of dust, there is little appreciable increase in  $\text{NO}_3^-$ . Note, the one green square indicates a sample that is likely to be predominantly sea salt, since it lies on the sea water slope shown in Figure 4. The blue circles have  $\text{NO}_3^-$  in excess of  $100 \text{ neq/m}^3$ , yet they are well away from the 1:1 line. Given their very high amount of  $\text{nss-Ca}^{2+}$ , it is likely that either the sample was obtained prior to the air mass reaching chemical equilibrium between the dust and  $\text{HNO}_3$ , or there was insufficient  $\text{HNO}_3$  to produce more particulate  $\text{NO}_3^-$ . The correlation between the black circles and  $\text{nss-Ca}^{2+}$  is even closer to 1:1 for  $\text{nss-SO}_4^{=}$  (Figure 6), than for  $\text{NO}_3^-$ . Again, there is little increase in  $\text{nss-SO}_4^{=}$  with increasing  $\text{nss-Ca}^{2+}$  for the red square population. The blue circles are still set apart with respect to  $\text{nss-SO}_4^{=}$  and  $\text{nss-Ca}^{2+}$ .  $\text{HNO}_3$  and  $\text{SO}_2$  (Figure 6), suggest the circles reflect the presence of higher levels of gas phase pollution

than is present for the red squares (or the non-dust-enhanced black solid squares).

Perhaps then, what is needed to enhance particulate phase  $\text{NO}_3^-$  and  $\text{SO}_4^{=}$  in the presence of dust, is a certain threshold of precursor gas phase species. From the figures shown here, this threshold appears to be around  $50 \text{ nmol/m}^3$  for  $\text{HNO}_3$ , and  $100 \text{ nmol/m}^3$  for  $\text{SO}_2$ , coupled with around  $100 \text{ neq/m}^3$  of  $\text{nss-Ca}^{2+}$  or more. However, the gas phase thresholds must be lower limits, since the mixing ratios of  $\text{HNO}_3$  and  $\text{SO}_2$  would have been higher further upstream, prior to their removal by reaction with the dust surfaces. Also recall, the  $\text{nss-Ca}^{2+}$  mixing ratios given here are likely to be underestimates, hence the threshold for  $\text{nss-Ca}^{2+}$  may be somewhat lower. Note, where  $\text{nss-Ca}^{2+}$  is low, there are still appreciable amounts of  $\text{nss-SO}_4^{=}$ . Presumably, this  $\text{nss-SO}_4^{=}$  is due to uptake of  $\text{nss-SO}_4^{=}$  on sea salts (coarse mode) or the presence of fine mode  $\text{NH}_4\text{HSO}_4$  and  $(\text{NH}_4)_2\text{SO}_4$ . These results are similar to those reported by Choi et al. [2001]. They also reported cases in Seoul where some dust events were enhanced in pollution species, while other events were not.

Next consider the relationship between  $\text{NO}_3^-$  and  $\text{NH}_4^+$  (Figure 7). There is a stunning correlation between these two species, with the data points lying along the 1:1 line indicative of  $\text{NH}_4\text{NO}_3$ . There is some excess of  $\text{NH}_4^+$  compared to the  $\text{NO}_3^-$ , but not much. This suggests that particulate  $\text{NO}_3^-$  is in fine rather than coarse mode. However, the relationship between  $\text{nss-SO}_4^{=}$  and  $\text{NH}_4^+$  (Figure 7) argues against this scenario. There is clearly more than enough  $\text{nss-SO}_4^{=}$  to accomodate all of the  $\text{NH}_4^+$ . Given the preferential formation of  $\text{NH}_4\text{HSO}_4$  and  $(\text{NH}_4)_2\text{SO}_4$  to that of the more volatile  $\text{NH}_4\text{NO}_3$  under atmospheric conditions, it seems unlikely that the bulk of  $\text{NH}_4^+$  is associated with

NO<sub>3</sub><sup>-</sup> in this region. The correlation observed here may be coincidental. There are very good correlations between NH<sub>4</sub><sup>+</sup> and both HNO<sub>3</sub> and SO<sub>2</sub> (Figure 7) suggesting that NH<sub>4</sub><sup>+</sup> is simply a good tracer for pollutants. Investigating this possibility further, there are excellent correlations between CO and NH<sub>4</sub><sup>+</sup> ( $R^2 = 0.94$ ) and Ethyne/CO and NH<sub>4</sub><sup>+</sup> ( $R^2 = 0.92$ ) for the dust sector data (Figure 8). Both of these, CO and Ethyne/CO, are used as tracers for pollution. Neither one plays any role in the formation of NH<sub>4</sub><sup>+</sup>, which supports the assertion that the good correlation between NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> seen here is coincidental. Although modeling work by Song and Carmichael [2001a] suggests that NH<sub>4</sub>NO<sub>3</sub> may well form along the “lower courses of the Huang River” which is indeed in the path of the dust flows, there is evidence suggesting that NO<sub>3</sub><sup>-</sup> is associated with the coarse mode. Wu and Okada [1994] found coarse NO<sub>3</sub><sup>-</sup> in all of their samples collected in Nagoya, Japan, including on the surface of dust particles during a Kosa event. Further, Kim and Park [2001] comparing samples during a dust storm and non-dust periods in Seoul, Korea, found the maximum concentration of NH<sub>4</sub><sup>+</sup> was in the fine mode (< 2 μm diameter) under both conditions. Meanwhile, both SO<sub>4</sub><sup>=</sup> and NO<sub>3</sub><sup>-</sup> were enhanced during the dust storm in the coarse fraction and were well correlated with coarse mode Ca<sup>2+</sup>. In plots of Kim and Park’s [2001] size resolved data, there is no evidence of a fine mode peak in NO<sub>3</sub><sup>-</sup>. In the absence of size resolved aerosol chemical measurements during TRACE-P, these observations argue against SO<sub>4</sub><sup>=</sup> and NO<sub>3</sub><sup>-</sup> being primarily associated with NH<sub>4</sub><sup>+</sup> in the presence of dust.

To estimate how much nss-SO<sub>4</sub><sup>=</sup> remains available for uptake on nss-Ca<sup>2+</sup>, assume all particulate NH<sub>4</sub><sup>+</sup> is in the form of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>. Then, measured NH<sub>4</sub><sup>+</sup> equivalence is

subtracted from measured  $\text{nss-SO}_4^-$  equivalence to yield excess  $\text{nss-SO}_4^-$  (Table 2). Further,  $\text{NO}_3^-$  is added to this excess  $\text{nss-SO}_4^-$  and the sum is compared to  $\text{nss-Ca}^{2+}$  (Table 2). On average, 57% of the available  $\text{nss-SO}_4^-$  can be taken up by  $\text{NH}_4^+$ , with the remainder available for uptake on dust and sea salt surfaces. Even including  $\text{NO}_3^-$ , there is ample  $\text{nss-Ca}^{2+}$  to take up the measured  $\text{NO}_3^-$  and excess  $\text{nss-SO}_4^-$ . Indeed, even if there were no  $\text{NH}_4^+$ , the available  $\text{nss-SO}_4^-$  and  $\text{NO}_3^-$  would only react with 76% of the available  $\text{nss-Ca}^{2+}$ . Clearly, the uptake of  $\text{nss-SO}_4^-$  and  $\text{NO}_3^-$  are limited by the amounts of  $\text{HNO}_3$  and  $\text{SO}_2$  present, not by dust. In comparison, in the NNW sector where dust is not so prevalent, there is insufficient  $\text{nss-Ca}^{2+}$  available to take up the available excess  $\text{nss-SO}_4^-$  and  $\text{NO}_3^-$  (Table 2). Here, these species are more likely to be associated with sea salt, and are present at much lower levels than observed in the dust sector. To further illustrate this, Figure 9 shows excess  $\text{nss-SO}_4^-$  versus  $\text{nss-Ca}^{2+}$ . If there was sufficient  $\text{nss-SO}_4^-$  to react with all of the  $\text{nss-Ca}^{2+}$  present, the data would fall along the 1:1 line. In fact, where dust is not enhanced, there is more  $\text{nss-SO}_4^-$  than can be accounted for by dust (black squares, Figure 9). This suggests this  $\text{SO}_4^-$  is associated with fine mode  $\text{NH}_4^+$ , or perhaps with coarse mode sea salt. However, where there is plenty of dust (circles and red squares, excess  $\text{nss-SO}_4^-$  is well correlated with  $\text{nss-Ca}^{2+}$  ( $R^2 = 0.87$ ) with a slope of 0.22. This again indicates that the uptake of  $\text{SO}_4^-$  on dust is limited by available  $\text{SO}_4^-$ , not dust. Further, when  $\text{NO}_3^-$  is included in this analysis, the most polluted samples are seen to lie along the 1:1 line (Figure 9), suggesting most of the  $\text{CO}_3^-$  in the dust has been displaced. For the remainder of the dust enhanced samples, the uptake appears to be limited by the availability of  $\text{HNO}_3$  and  $\text{SO}_2$ .

This exercise probably underestimates the amount of excess  $\text{nss-SO}_4^-$ . It has been assumed that the equivalence ratio of  $\text{NH}_4^+$  to  $\text{nss-SO}_4^-$  is 1. However, in measurements made in Seoul during dust conditions [Kim and Park, 2001], the fine mode ratio of  $\text{NH}_4^+$  to  $\text{SO}_4^-$  was found to be 0.6. Hence it is likely that the amount of excess  $\text{nss-SO}_4^-$  has been underestimated here somewhat, which would result in higher slopes of the relationships shown in Figure 9. And as noted earlier, the non-sea-salt fractions themselves have been underestimated, since some component of the  $\text{Na}^+$  present is due to dust, even though it is all assumed to be sea salt. Thus, the total amounts of species in non-sea-salt fractions is somewhat higher than that shown here. Another issue to bear in mind comes from a study of individual particle composition. Gao and Anderson [2001] reported fly ash particles (distinguishable from dust by their spherical rather than irregular shape) also show aggregation with  $\text{CaSO}_4$ . This is attributed to the use of  $\text{CaCO}_3$  to scrub  $\text{SO}_2$  from stack emissions. This can confound the interpretation of non-size resolved aerosol chemistry, because there will be a component of the  $\text{nss-Ca}^{2+}$  in the fine fraction which is not related to dust. However, in the presence of large dust outbreaks, it is expected that this contribution to the total  $\text{nss-Ca}^{2+}$  will be small.

Finally, the partitioning between particulate  $\text{NO}_3^-$  ( $\text{p-NO}_3^-$ ) and gas phase  $\text{HNO}_3$  is shown for dust (Channel) versus non-dust (NNW) sectors (Figure 10). For comparison, the partitioning is also shown for the other two sectors studied during TRACE-P, SE Asia and WSW (see Jordan et al., this issue for a complete description of these sectors). The green diamonds show the means (center horizontal line) with the 95% confidence interval indicated by the upper and lower points of the diamonds, while the width of the diamond

is proportional to the group size. The red boxes show the quantiles, with the upper and lower bars indicating the 90<sup>th</sup> and 10<sup>th</sup> percentiles, respectively, the top and bottom of the box are at the 75<sup>th</sup> and 25<sup>th</sup> percentiles, respectively, and the red line in the box is the median. The circles to the right indicate whether the means are statistically different. The center of each circle is aligned with the mean of its respective group, the diameter of the circle spans the 95% confidence level. When the circles do not overlap, the means are significantly different. When they do overlap the means may not be significantly different. Here we see that while the means for SE Asia and WSW may not be significantly different from each other, they are both significantly different from the other two, which are also significantly different from each other (Figure 10). For the groups least effected by the presence of sea salt and dust the amount  $\text{p-NO}_3^-$  accounts for only 6 – 13% of the total  $\text{NO}_3^-$  ( $\text{t-NO}_3^- = \text{p-NO}_3^- + \text{HNO}_3$ ) present, on average (Table 3). Where dust is not a dominant component of the atmosphere (NNW)  $\text{p-NO}_3^-$  accounts for 37% of the  $\text{t-NO}_3^-$  on average, probably due to the influence of sea salts in this sector. For the dust sector,  $\text{p-NO}_3^-$  makes up 54% of the total on average, with maximum values of 72% observed (Table 3). These numbers agree well with those predicted by Song and Carmichael [2001a] where 10-50% of  $\text{t-NO}_3^-$  would be particulate in the presence of dust and sea salts, with >70% in dust and sea salt plume centers in the boundary layer, while in the free troposphere, 10-30% would be  $\text{p-NO}_3^-$  on sea salts and >50% in dust plume centers.

## SUMMARY



Dust storms are prevalent in East Asia, with the dust being carried downwind along well defined routes [Sun et al., 2001]. This dust starts out with very little  $\text{NO}_3^-$  or  $\text{SO}_4^{=}$  in the dust grains [Nishikawa et al., 1991; and Zhang and Iwasaka, 1999]. However, in the presence of pollution, these dust particles can take up  $\text{NO}_3^-$  and  $\text{SO}_4^{=}$ , altering both the partitioning between particulate and gas phases of these species, as well as their size distributions in the atmosphere (especially,  $\text{SO}_4^{=}$ ). During the TRACE-P mission, dust was found to be well confined to a particular sector emanating from Asia in good agreement with the routes described by Sun et al., [2001].

This dust sector also contained the highest mixing ratios of pollutant species observed, with gas-phase  $\text{HNO}_3$  2.7 times higher on average than in the adjacent non-dust sector. Similarly,  $\text{SO}_2$ , CO, and the ratio of Ethyne/CO were 6.2, 1.5, and 1.1 times higher in the dust samples. Sea salt could not account for the enhancements in  $\text{NO}_3^-$  and  $\text{SO}_4^{=}$  (factors of 5.7 and 2.6, respectively), since the mean mixing ratios of  $\text{Na}^+$  in the dust and non-dust regions were comparable (64 and 57  $\text{nmol/m}^3$ , respectively). Although a good correlation between  $\text{NO}_3^-$  and  $\text{NH}_4^+$  was observed, it appears that this was coincidental. As tracer of anthropogenic species,  $\text{NH}_4^+$  also exhibited excellent correlations with CO and the Ethyne/CO ratio (0.94 and 0.92, respectively). These species are not involved in any way with  $\text{NH}_4^+$  formation. Prior observations in east Asia where size resolved data was available did not show fine mode peaks of  $\text{NO}_3^-$  when dust was present. Further, calculations showed that there is ample nss- $\text{SO}_4^{=}$  to occupy the available  $\text{NH}_4^+$  and still have enough left over to react with dust.

The uptake of  $\text{NO}_3^-$  and  $\text{SO}_4^{=}$  appears to be limited by the availability of gas phase species, with the lower limits of these thresholds found here to be  $50 \text{ nmol/m}^3 \text{ HNO}_3$  and  $100 \text{ nmol/m}^3 \text{ SO}_2$ . Little uptake by dust occurs below these thresholds. Above them, the uptake of  $\text{NO}_3^-$  and  $\text{SO}_4^{=}$  can be substantial and in some cases may entirely drive off the  $\text{CO}_3^{=}$  in the dust aerosol. This has implications for the removal of these species from the atmosphere in this region, since coarse mode aerosols are much more readily removed than fine mode. The partitioning between particulate and gas-phase  $\text{NO}_3^-$  shows 54% of the total  $\text{NO}_3^-$  (t- $\text{NO}_3^-$ ) in the dust sector is in particulate (p- $\text{NO}_3^-$ ) phase on average. In some samples, p- $\text{NO}_3^-$  exceeded 70%. This is in good agreement with model predictions Song and Carmichael [2001a]. In the non-dust sector, p- $\text{NO}_3^-$  constituted 37% of t- $\text{NO}_3^-$ , likely due to the heavy influence of sea salt. The two other sectors analyzed previously [Jordan et al., this issue] show little influence of dust or sea salt, which results in p- $\text{NO}_3^-$  contributing a small fraction to the total,  $< 15\%$ . This also has implications for the enhanced removal of nitrogen from the atmosphere in the presence of dust.

## ACKNOWLEDGMENTS

The authors wish to thank the NASA Global Tropospheric Chemistry Program and the National Research Council for their support of this work.

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## FIGURE CAPTIONS

**Figure 1.** Map of cold air outbreaks and suspended dust routes in east Asia, from Sun et al., [2001].

**Figure 2.** Back trajectories of the dust sector (Channel, green) and the non-dust sector (NNW, red).

**Figure 3.** Mean aerosol mixing ratios for NNW and Channel sectors.

**Figure 4.**  $\text{Mg}^{2+}$  versus  $\text{Na}^+$ .

**Figure 5.** Aerosol and  $\text{HNO}_3$  mixing ratios shown as a function of altitude. The density ellipses enclose 90% of the points within their respective groups.

**Figure 6.**  $\text{NO}_3^-$ ,  $\text{nss-SO}_4^{=}$ ,  $\text{HNO}_3$ , and  $\text{SO}_2$  shown as a function of dust ( $\text{nss-Ca}^{2+}$ ).

Circles indicate dust samples with enhanced  $\text{NO}_3^-$  and  $\text{nss-SO}_4^{=}$ . Squares indicate dust samples without enhanced pollution species.

**Figure 7.**  $\text{NO}_3^-$ ,  $\text{nss-SO}_4^{=}$ ,  $\text{HNO}_3$ , and  $\text{SO}_2$  shown as a function of  $\text{NH}_4^+$ . Circles indicate dust samples with enhanced  $\text{NO}_3^-$  and  $\text{nss-SO}_4^{=}$ . Squares indicate dust samples without enhanced pollution species.

**Figure 8.** CO and Ethyne/CO versus  $\text{NH}_4^+$ . All data from NNW and Channel are plotted, but only those from Channel are used for the linear fits.

**Figure 9.** Excess  $\text{nss-SO}_4^-$  and excess  $\text{nss-SO}_4^- + \text{NO}_3^-$  versus  $\text{nss-Ca}^{2+}$  show how much of these species are available for uptake by dust after allowing  $\text{NH}_4^+$  to take up as much  $\text{nss-SO}_4^-$  as possible.

**Figure 10.** Comparison of  $\text{NO}_3^-$  partitioning between the dust sector (Channel), a sector with a lot of sea salt (NNW), and two sectors where the influence of dust and sea salt are minimal (SE Asia and WSW).



**Table 1.** Means, standard deviations, medians, minima, maxima, and number of samples for various aerosol and gas phase species.

|                | $\text{NO}_3^-$<br>(nmol/m <sup>3</sup> ) | nss- $\text{SO}_4^{=}$<br>(nmol/m <sup>3</sup> ) | nss- $\text{Ca}^{2+}$<br>(nmol/m <sup>3</sup> ) | $\text{Na}^+$<br>(nmol/m <sup>3</sup> ) | $\text{NH}_4^+$<br>(nmol/m <sup>3</sup> ) | $\text{HNO}_3$<br>(nmol/m <sup>3</sup> ) | $\text{SO}_2$<br>(nmol/m <sup>3</sup> ) | $\text{CO}$<br>(ppbv) | Ethyne/ $\text{CO}$<br>(pptv/ppbv) |
|----------------|---|--|---|---|---|--|---|-----------------------|------------------------------------|
| <b>Channel</b> | 74±110                                    | 91±91  | 168±177   | 64±91                                   | 104±115                                   | 44±49                                    | 147±173                                 | 258±138               | 3.3±1.1                            |
|                | 40 (1-60)                                 | 78 (5-491)                                       | 115 (2-622)                                     | 26 (1-314)                              | 92 (6-639)                                | 33(6-264)                                | 115(1-931)                              | 256 (109-830)         | 3.2 (1.9-8.0)                      |
|                | 38  | 38   | 38  | 38                                      | 38  | 38                                       | 33                                      | 38                    | 38                                 |
| <b>NNW</b>     | 13±16                                     | 35±26  | 10±12   | 57±70                                   | 38±29                                     | 17±13                                    | 24±36                                   | 176±49                | 3.0±0.8                            |
|                | 6 (1-90)                                  | 31 (3-96)  | 5 (0-59)  | 12 (1-255)                              | 26 (1-101)                                | 17(3-61)                                 | 8(1-174)                                | 185 (43-266)          | 3.1 (0.9-4.6)                      |
|                | 77  | 77   | 77  | 77                                      | 77  | 76                                       | 62                                      | 77                    | 75                                 |

**Table 2.** Means, standard deviations, medians, minima, maxima, and number of samples for excess nss-SO<sub>4</sub><sup>=</sup> and NO<sub>3</sub><sup>-</sup> compared to available dust.

|                | nss-SO <sub>4</sub> <sup>=</sup><br>(neq/m <sup>3</sup> ) | NH <sub>4</sub> <sup>+</sup><br>(neq/m <sup>3</sup> ) | Excess nss-SO <sub>4</sub> <sup>=</sup><br>(neq/m <sup>3</sup> ) | NO <sub>3</sub> <sup>-</sup><br>(neq/m <sup>3</sup> ) | Excess nss-SO <sub>4</sub> <sup>=</sup> + NO <sub>3</sub> <sup>-</sup><br>(neq/m <sup>3</sup> ) | nss-Ca <sup>2+</sup><br>(neq/m <sup>3</sup> ) |
|----------------|---|---|--|---|---|---|
| <b>Channel</b> | 182±183<br>156 (11-982)<br>38                             | 104±115<br>92 (6-639)<br>38                           | 78±84<br>58 (0-343)<br>38  | 74±110<br>40 (1-60)<br>38                             | 152±178<br>103 (6-945)<br>38  | 335±353<br>229 (4-1245)<br>38                 |
| <b>NNW</b>     | 70±52<br>62 (6-191)<br>77                                 | 38±29<br>26 (1-101)<br>77                             | 32±28<br>23 (3-98)<br>77   | 13±16<br>6 (1-90)<br>77                               | 45±37<br>39 (3-128)<br>77   | 19±24<br>12 (0-119)<br>74                     |

**Table 3.** Means, standard deviations, medians, minima, maxima, and number of samples for nitrate partition comparison  $\text{NO}_3^-/(\text{NO}_3^- + \text{HNO}_3)$

| <b>NNW</b>       | <b>Channel</b>   | <b>WSW</b>       | <b>SE Asia</b>   |
|------------------|------------------|------------------|------------------|
| 0.37±0.16        | 0.54±0.15        | 0.13±0.13        | 0.06±0.05        |
| 0.40 (0.00-0.63) | 0.57 (0.08-0.72) | 0.06 (0.00-0.43) | 0.04 (0.00-0.18) |
| 76               | 38               | 43               | 26               |